한국환경과학회지 제21권(제6호), 655～659, 2012
Journal of the Environmental Sciences

http://dx.doi.org/10.5322/JES.2012.21.6.655

COD Removal of Rhodamine B from Aqueous Solution by Electrochemical Treatment

Dong-Seog Kim, Young-Seek Park[1)*]

Department of Environmental Science, Catholic University of Daegu, Gyeongbuk 712-702, Korea
[1)]Faculty of Liberal Education, Daegu University, Gyeongbuk 712-714, Korea

(Manuscript received 13 January, 2012; revised 23 March, 2012; accepted 14 May, 2012)

Abstract

This study elucidates the COD removal of dye (Rhodamine B) through electrochemical reaction. Effects of current density (7.2 to 43.3 mA/cm^2), electrolyte type (NaCl, KCl, Na_2SO_4, HCl), electrolyte concentration (0.5 to 2.0 g/L), air flow rate (0 to 4 L/min) and pH (3 to 11) on the COD removal of Rhodamine B were investigated. The observed results showed that the increase of pH decrease the COD removal efficiency. Whereas, the increase of current density, NaCl concentration and air flow rate caused the increase of the COD removal of Rhodamine B.

Key Words : COD removal, Electrochemical treatment, Rhodamine B, Ru-Sn-Sb electrode

1. Introduction

Textile industry produce considerable water pollution problem by discharging effluents. The effluent of textile industry process contains various types of pollutants such as dyes, detergents, surfactants and suspended solids (Robert et al., 2007). The effluent in textile industry has often been discharged over the discharge limit when it is treated only by the conventional treatment process such as the connected chemical and biological process, because the wastewater in textile industry has many recalcitrant materials.

Therefore, the research for the advanced oxidation processes (AOPs) such as electron beam, Fenton oxidation, ozone oxidation, photo-catalytic and electrochemical processes is needed for the stable treatment of textile industry wastewater.

Especially, the electrochemical oxidation process is evaluated as an alternative to solve the problem generated by the textile industry effluent. Electrochemical oxidation is a complex reaction involving coupling of electron transfer reaction. Therefore, the electrolytes present in wastewater dissociate into ions and oxidation of electrons occurs at the anode. Several researchers have investigated the feasibility of electrochemical degradation of dyes with various electrode materials for wastewater treatment such as titanium-based electrodes (Rajeshwar and Ibanez, 1997; Szpyrkowicz et al., 2000), platinum electrode (Sanroman et al., 2004), diamond and metal alloy electrodes (Rivera et al., 2004), and boron doped diamond electrodes (Chen et al, 2003; Fernandes et al., 2004). Applications of electrochemical method for textile wastewater have been tested and a good removal efficiency of organic substances at various operating conditions is obtained (Lin and Feng, 1994; Osutveren and Koparal, 1994).

This paper concerns with the study of current density, electrolyte type, electrolyte concentration, air flow rate and pH which are the main parameters that

*Corresponding author : Young-Seek Park, Faculty of Liberal Education, Daegu University, Gyeongbuk 712-830, Korea
Phone: +82-53-850-4571
E-mail: ysparkk@daegu.ac.kr

influences the performance of the electrochemical oxidation process in textile wastewater on laboratory scale.

2. Materials and Methods

Electrochemical reactor used in this study is consisted of Ru-Sn-Sb oxide coated titanium mesh electrodes (11 cm x 6.3 cm). The mesh type anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 2 mm. The experiments were done using 1.0 L of Rhodamine B (RhB) dye solution with constant stirring at 150 ~ 200 rpm with a magnetic stirrer to maintain uniformity in a reactor. The area of electrode exposed for the electrolysis was fixed to be 69.3 cm^2.

Chemical oxygen demand (COD) value for the RhB sample before and after electrolysis was measured using Standard methods (APH-AWWA-WPCE, 1992).

3. Results and Discussion

3.1. Effect of current density

Fig. 1 shows the COD removal efficiency with different current density in electrochemical process. The current density was varied from 7.2 to 43.3 mA/cm^2 using 1.0 g/L NaCl as electrolyte and 2.0 L/min air flow rate at pH 7. The COD removal efficiency increased by increasing the current density because the increment of current density increase the generation of several oxidants (O_3, free chlorine, ClO_2, H_2O_2, OH radical etc., Kim and Park, 2009).

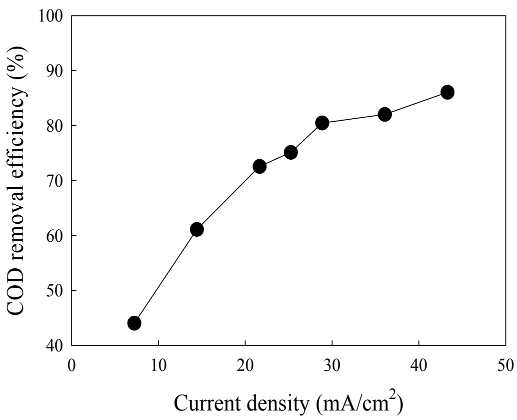

Fig. 1. Effect of current density on the COD removal efficiency in electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, NaCl concentration 1.0 g/L, air flow rate 2.0 L/min).

3.2. Effect of electrolyte type

Fig. 2 shows the effect of electrolyte type (NaCl, KCl, Na_2SO_4, HCl) on the COD removal efficiency in electrochemical process. The COD removal efficiency using NaCl as an electrolyte was higher than that using any other electrolyte. And the COD removal efficiencies with Na_2SO_4 and HCl were low, which was similar with study of Li et al (2005). It was suggested by Li et al (2005) that NaCl, which could be oxidized to form a strong oxidant of HOCl, could promote the degradation of phenol. Also, in this study, the production of other oxidants (O_3, H_2O_2, ClO_2 etc.) using NaCl was much higher than that using Na_2SO_4 or HCl (Kim and Park, 2009), which showed that the NaCl was the best electrolyte in

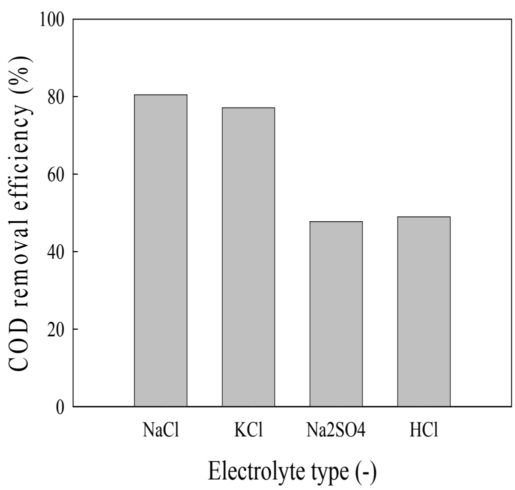

Fig. 2. Effect of electrolyte type on the COD removal efficiency in electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm^2, air flow rate 2.0 L/min).

the COD removal using electrochemical reaction. Li et al (2009) showed that phenol in Na_2SO_4 decreased from 490 mg/L to 0 mg/L in 35h with Ti/RuO_2 at the current density of 20 mA/cm^2. However, phenol solution with 1.0 g/L NaCl as supporting electrolyte was degraded from 80 mg/L to 0 mg/L within 130 min at the current density of 10 mA/cm^2 (Li et al, 2009). Therefore, we can see that the NaCl presence is necessary for the efficient degradation of recalcitrant materials such as RhB or phenol.

3.3. Effect of NaCl concentration

In order to investigate the effect of electrolyte concentration on the COD removal, NaCl concentration was varied from 0.5 to 2.0 g/L using current density 28.9 mA/cm^2 and 2.0 L/min air flow rate at pH 7.0. The results are presented in Fig. 3. The COD removal efficiency was increased by increasing the NaCl concentration due to the increased mass transport of chloride ions to the anode surface and also increased diffusion in the diffusion layer of the anode. As a result, more amount of several oxidants were generated (Kim and Park, 2009), which results in the increased COD removal efficiency.

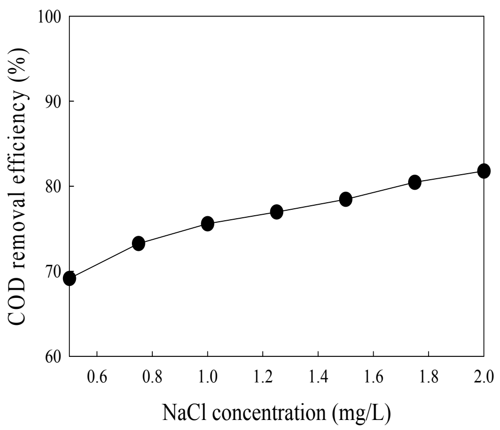

Fig. 3. Effect of NaCl concentration on the COD removal efficiency in electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm^2, air flow rate 2.0 L/min).

3.4. Effect of air flow rate

For enhancing COD removal efficiency, the input of air was adjusted. Effect of air flow rate on the COD removal efficiency is illustrated in Fig. 4. It appears that the COD removal efficiency in the air flow rate of 3.0 L/min was a little higher than that of 0, 1.0 and 2.0 L/min. Nonetheless, a similar COD removal efficiency was found between that of 3.0 and 4.0 L/min, which mean that the aeration process is not an economical choice for the enhancement of COD removal efficiency regardless of accelerating mass transfer when the air flow rate was over 3.0 L/min. The observation in our experiments was in agreement with that reported by Chen and Liang (2009), who stated that the production of electro-generated H_2O_2 was proportional to the mass transfer rate of dissolved oxygen to the cathode surface. By the report of Chen and Liang (2009), it indicated that the TOC removal efficiencies in electrochemical reaction with out dosage of oxygen were slightly lower than those with dosage of oxygen.

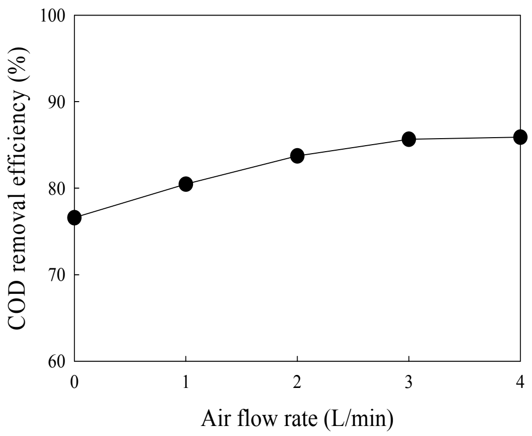

Fig. 4. Effect of air flow rate on the COD removal efficiency in electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm^2, NaCl concentration 1.0 g/L).

3.5. Effect of pH

The COD removal efficiency decreased with increasing in the initial pH of the solution as shown in Fig. 5. The COD removal efficiency decreased drastically as the initial pH was 11.0. The chlorine/hypochlorite generation was stable at given current density. However, at higher pH value the hypochlorite acid converts itself into chlorate or hypochlorate according to the reactions mentioned in eqs. (1) and (2). This results in the reduced availability of hypochlorite at higher pH which causes reduction in COD removal.

$$6HOCl + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^- \quad (1)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \quad (2)$$

Another reason may be at acid pH, the chlorine is present in the solution in the form of hypochlorous acid, which is having higher oxidation potential (1.49 V) than that of hypochlorite (0.94 V) (Prasad and Srivastava, 2009). The hypochlorite is prevalent in the alkaline condition (Szpyrkowicz et al., 2000).

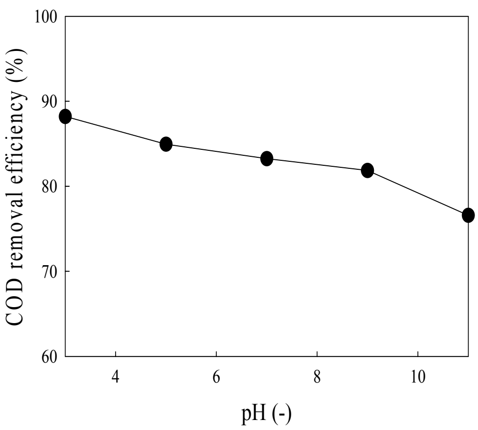

Fig. 5. Effect of initial pH on the COD removal efficiency in electrochemical process using Ru-Sn-Sb electrodes (Operating conditions : current density 28.9 mA/cm^2, NaCl concentration 1.0 g/L, air flow rate 2.0 L/min).

4. Conclusion

This study demonstrated the usefulness of electrochemical COD treatment using Ru-Sn-Sb oxide electrode. The effects of 4 factors (current density, NaCl concentration, air flow rate, pH) on COD removal were studied. COD removal efficiency increased by the increasing the current density and NaCl concentration. It decreased by the increasing pH value by increasing the pH value. However, air flow rate had no great effect on the COD removal efficiency. COD removal efficiency using NaCl as an electrolyte was higher than that using any other electrolyte.

Acknowledgements

This work was supported by research grants from the Catholic University of Daegu in 2010.

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